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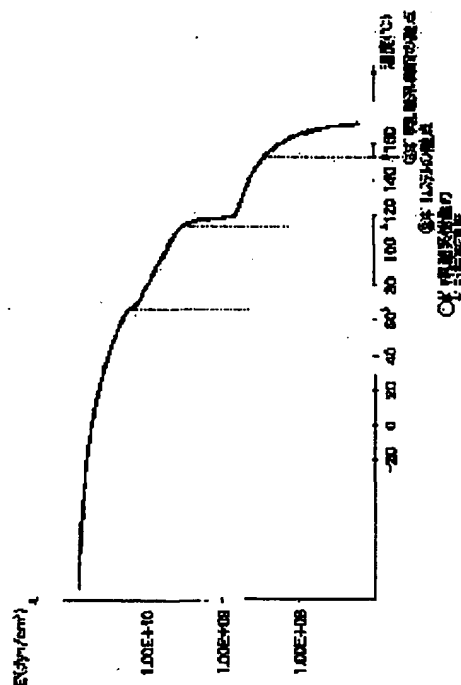
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(54) BIODEGRADABLE SHEET, FABRICATED ARTICLE USING SHEET AND PROCESS FOR FABRICATED SHEET

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a biodegradable sheet that has good fabricability and can produce an article in heat resistance without needing at a high processing temperature.

SOLUTION: The biodegradable sheet is produced by precrystallizing a sheet formed from a resin composition which comprises 75-25 wt.% polylactic acid- base resin and 25-75 wt.% polyester having a glass transition temperature of not more than 0° C and a melting point of not less than 90° C to a temperature not more than a melting point of the polylactic acid resin.



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CLAIMS

[Claim(s)]

[Claim 1] The biodegradability sheet characterized by carrying out preliminary crystallization of the sheet which consists of the resin constituent which blended 75 - 25 % of the weight of polylactic acid system resin, and 25 - 75 % of the weight of polyester 0 degree C or less and the melting point of glass transition temperature are higher than the glass transition temperature of said polylactic acid system resin, and it is [polyester] below the melting point of polylactic acid system resin so that it might become 100 % of the weight in total.

[Claim 2] The biodegradability sheet with which 75 - 25 % of the weight of polylactic acid system resin and glass transition temperature are characterized by 0 degree C or less and the melting point carrying out preliminary crystallization of the sheet which consists of the resin constituent which blended 25 - 75 % of the weight of polyester which is below the melting point of polylactic acid system resin above 90 degrees C so that it might become 100 % of the weight in total.

[Claim 3] The biodegradability sheet according to claim 1 or 2 characterized by said polyester being biodegradability aliphatic series system polyester other than polylactic acid system resin.

[Claim 4] A biodegradability sheet given in any 1 term of claims 1-3 characterized by being at least one sort chosen from the group which said biodegradability aliphatic series system polyester becomes from the copolymer of polybutylene succinate, a polybutylene succinate horse mackerel peat, polybutylene horse mackerel peat terephthalate, polyglycolic acid, polyester carbonate, polyhydroxy butyrate, and polyhydroxy BARIRETO, and the copolymer of polyhydroxy butyrate and polyhydroxy hexanoate.

[Claim 5] A biodegradability sheet given in any 1 term of claims 1-4 characterized by the degree of crystallinity after preliminary crystallization of said polylactic acid system resin being 20% or more.

[Claim 6] The shaping approach of the biodegradability sheet characterized by fabricating a biodegradability sheet according to claim 1 to 5 at the temperature of more than the melting point of aliphatic series system polyester, and under the melting point of polylactic acid system resin.

[Claim 7] The Plastic solid of the biodegradability sheet characterized by being fabricated by the shaping approach according to claim 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the biodegradability sheet and Plastic solid which were excellent in the moldability especially about the Plastic solid which used a biodegradability sheet and this sheet, and its shaping approach, and its shaping approach.

[0002]

[Description of the Prior Art] Polyethylene, polypropylene, a polyvinyl chloride, polystyrene, polyethylene terephthalate, etc. have been used as ingredients, such as food containers, such as a cup and a tray, a blister pack and the container for hot philharmonics or a tray for electronic-parts conveyance, and a carrier tape. Generally these plastics etc. are thrown away, and after use, in case it discards, disposal of incineration or reclamation poses a problem. Resin, such as polyethylene, polypropylene, and polystyrene, has much calorific value at the time of combustion, and has a possibility of frying an incinerator during combustion processing, and a polyvinyl chloride generates gas harmful at the time of incineration. On the other hand, also in a landfill, since chemical stability is high, it will hardly be decomposed under natural environment, but these plastics will remain in soil semipermanently, and will saturate the capacity of a refuse disposal lot for a short period of time. Moreover, if abandoned in natural environment, a scene will be spoiled or the living environment of a marine organism etc. will be destroyed. Then, in recent years, research of the ingredient of biodegradability and development are actively performed from a viewpoint of environmental protection. There is polylactic acid as one of the ingredients of the biodegradability which attracts attention. Since it is biodegradability, hydrolysis advances automatically by the inside of soil, or underwater, and polylactic acid system resin serves as a harmless decomposition product by the microorganism. Moreover, a furnace is not hurt even if it performs incineration disposal, since the amount of heat of combustion is small. Furthermore, since a start raw material is the vegetable origin, it also has the features of being able to free oneself from drained petroleum resources.

[0003] However, the container for pouring in a container and boiling water into which polylactic acid system resin has low thermal resistance, and heating food is put etc. did not fit use in an elevated temperature. Moreover, since it was not rare to reach an elevated temperature, either, if a storage shed, the truck under transportation, and the interior of a ship become a summer etc. when storing and conveying the sheet made of polylactic acid system resin, and its Plastic solid, problems, such as deformation and welding, might occur.

[0004] As a technique which gives thermal resistance to polylactic acid system resin, in a forming cycle, metal mold is held near the crystallization temperature of polylactic acid system resin (80-130 degrees C), and there is the approach of giving thermal resistance by making altitude crystallize polylactic acid within metal mold. However, in order to crystallize the polylactic acid fabricated by this approach within metal mold, while crystallization is completed, a Plastic solid must be held within metal mold, rather than the usual shaping, a molding cycle becomes long and a manufacturing cost becomes high. since [moreover,] it is necessary to warm metal mold -- warming -- a facility is also required.

[0005] Moreover, there is the approach of giving thermal resistance by carrying out annealing treatment after shaping and making altitude back-crystallize polylactic acid system resin. However, by this approach, a Plastic solid deforms the Plastic solid of polylactic acid system resin in the back-crystallized process, and since the process which makes dimensional accuracy produce and back-crystallize a problem is required, a manufacturing cost becomes high.

[0006] After making JP,8-73628,A carry out preliminary crystallization of the lactic-acid system polymer sheet which uses polylactic acid as a principal component by annealing processing and making a storage modulus into the predetermined range at it as an option which gives thermal resistance to polylactic acid system resin, the approach of fabricating with the heated metal mold is indicated. However, in order to acquire a Plastic solid with thermal resistance, the facility which needs to hold the temperature of metal mold near the crystallization temperature of polylactic acid system resin (80-130 degrees C), and it is necessary to make complete crystallization of polylactic acid system resin within metal mold, and warms metal mold is also required of this approach. Moreover, by this approach, rather than the usual shaping, a molding cycle becomes long and a manufacturing cost becomes high.

[0007]

[Problem(s) to be Solved by the Invention] This invention is made that the above-mentioned trouble should be solved, the purpose of this invention does not generate an environmental problem, and it excels in thermal resistance, and fabrication nature is good and is to offer the biodegradability sheet which can be fabricated simply. Moreover, it is in the Plastic solid using this biodegradability sheet, and offering that shaping approach.

[0008]

[Means for Solving the Problem] 0 degree C or less and the melting point have 75 - 25 % of the weight of polylactic acid system resin, and a glass transition temperature higher than the glass transition temperature of said polylactic acid system resin, and the biodegradability sheet of this invention is characterized by carrying out preliminary crystallization of the sheet which consists of the resin constituent which blended 25 - 75 % of the weight of polyester which is below the melting point of polylactic acid system resin so that it might become 100 % of the weight in total. another voice of this invention -- a biodegradability sheet [like] is characterized by 75 - 25 % of the weight of polylactic acid system resin and glass transition temperature carrying out preliminary crystallization of the sheet which consists of the resin constituent which blended 25 - 75 % of the weight of polyester 0 degree C or less and whose melting point are below the melting points of polylactic acid system resin above 90 degrees C so that it might become 100 % of the weight in total. Here, as for said polyester, it is desirable that it is biodegradability aliphatic series system polyester other than polylactic acid system resin. Moreover, said biodegradability aliphatic series system polyester can be at least one sort chosen from the group which consists of a copolymer of polybutylene succinate, a polybutylene succinate horse mackerel peat, polybutylene horse mackerel peat terephthalate, polyglycolic acid, polyester carbonate, polyhydroxy butyrate, and polyhydroxy BARIRETO, and a copolymer of polyhydroxy butyrate and polyhydroxy hexanoate. Moreover, the degree of crystallinity after preliminary crystallization of said polylactic acid system resin can be 20% or more. The shaping approach of the biodegradation sheet of this invention is characterized by fabricating the above-mentioned biodegradability sheet at the temperature of more than the melting point of aliphatic series system polyester, and under the melting point of polylactic acid system resin. The Plastic solid of the biodegradation sheet of this invention is characterized by being fabricated by the above-mentioned shaping approach.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The biodegradability sheet of this invention forms a sheet from the resin constituent containing 75 - 25 % of the weight of polylactic acid system resin, and a 25 - 75 % of the weight [of specific polyester] compound, and carries out preliminary crystallization. As for the weight ratio of polylactic acid system resin and polyester, it is desirable to blend the 25 - 75 % of the weight of the above-mentioned polyester with 75 - 25 % of the weight of polylactic acid system resin so that it may become 100 % of the weight in total. If the loadings of polylactic acid system resin exceed 75 % of the weight, fabrication nature will worsen

and general-purpose shaping of a vacuum forming, pressure forming, etc. will become difficult. Moreover, at 25 or less % of the weight, a result in which the rigidity of the sheet obtained and a Plastic solid is inferior is brought.

[0010] As polylactic acid system resin used for this invention, the homopolymer whose structural unit is L-lactic acid or D-lactic acid, i.e., Pori, (L-lactic acid), Pori (D-lactic acid) and the copolymer whose structural units are both L-lactic acid and D-lactic acid, i.e., Pori, (DL-lactic acid), and these mixtures are mentioned. As a polymerization method of polylactic acid system resin, which well-known approaches, such as a condensation polymerization method and a ring-opening-polymerization method, are employable. for example, a condensation polymerization method -- if -- the polylactic acid system resin which carries out direct dehydration condensation polymerization of L-lactic acid, D-lactic acids, or such mixture, and has the presentation of arbitration can be obtained. Moreover, by the ring-opening-polymerization method, polylactic acid system resin can be obtained using the catalyst suitably chosen in the lactide which is the annular dimer of a lactic acid while using the modifier etc. if needed. There are L-lactide which is the dimer of L-lactic acid, D-lactide which is the dimer of D-lactic acid, and a DL-lactide which consists of L-lactic acid and a D-lactic acid further as lactide, and the polylactic acid system resin which has the presentation of arbitration and crystallinity can be obtained by mixing and carrying out the polymerization of these if needed.

[0011] Furthermore, if needed [, such as heat-resistant improvement], a little copolymerization component can also be added and non-aliphatic series diols, such as non-aliphatic series dicarboxylic acid, such as a terephthalic acid, and an ethyleneoxide addition product of bisphenol A, etc. can also be used. A small amount of chain elongation agent, for example, a diisocyanate compound, an epoxy compound, an acid anhydride, etc. can also be used for the purpose of molecular-weight increase further again.

[0012] Polylactic acid system resin may be a copolymer with other hydroxycarboxylic acid units, such as alpha-hydroxycarboxylic acid, further, or may be a copolymer with aliphatic series diol / aliphatic series dicarboxylic acid. As other hydroxycarboxylic acid units, lactone, such as 2 organic-functions aliphatic series hydroxycarboxylic acid and caprolactones, such as optical-isomer [of a lactic acid] (to L-lactic acid, it is L-lactic acid to D-lactic-acid and D-lactic acid), glycolic-acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, 2-hydroxy-n-butanoic acid, 2-hydroxy 3, and 3-dimethyl butanoic acid, 2-hydroxy 3-methyl butanoic acid, 2-methyl lactic acid, and a 2-hydroxy caproic acid, a butyrolactone, and a valerolactone, is mentioned. As aliphatic series diol by which copolymerization is carried out to polylactic acid system resin, ethylene glycol, 1,4-butanediol, 1, and 4-cyclohexane dimethanol etc. is mentioned. Moreover, as aliphatic series dicarboxylic acid, a succinic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc. are mentioned.

[0013] It is desirable still more desirable that it is within the limits of 50,000-400,000, and the weight average molecular weight of polylactic acid system resin is 100,000-250,000. If the weight average molecular weight of polylactic acid system resin is less than 50,000, practical use physical properties will be hard to be discovered, and when it exceeds from 400,000, melt viscosity is too high and may be inferior to fabrication nature.

[0014] It is required to blend specific polyester in this invention in order to give thermal resistance, shock resistance, and fabrication nature to a sheet and its Plastic solid. Specific polyester has a glass transition temperature higher than the glass transition temperature of the polylactic acid system resin which 0 degree C or less and the melting point blend, for example, it is polyester below the melting point of 90 degrees C or more and polylactic acid system resin. If glass transition temperature is higher than 0 degree C, the shock-proof amelioration effectiveness will become inadequate. Moreover, if the melting point is lower than 90 degrees C, it may become what has the inadequate thermal resistance of a Plastic solid. In this invention, although the glass transition temperature (Tg) of polyester needs to be 0 degree C or less, it is desirable that it is -20 degrees C or less. In addition, although the melting point of polylactic acid system resin changes with mixed rates of L-lactic acid and D-lactic acid which are structural units, generally it is about 135 degrees C - 175 degrees C. If higher than the melting point of the polylactic acid system resin which the melting point of polyester blends, the semantics which carries

out preliminary crystallization of the polylactic acid system resin will be lost, and a problem will arise in respect of rigidity or fabrication nature.

[0015] In this invention, it is desirable as polyester to use biodegradability aliphatic series system polyester other than a polylactic acid system polymer. The aliphatic series polyester obtained as biodegradability aliphatic series system polyester by condensing a polyhydroxy carboxylic acid, aliphatic series diol and aliphatic series dicarboxylic acid, or aromatic series dicarboxylic acid or aliphatic series aromatic polyester, the aliphatic series polyester which carried out ring opening polymerization of the annular lactone, synthetic system aliphatic series polyester, the aliphatic series polyester by which a biosynthesis is carried out within a fungus body are mentioned.

[0016] As a polyhydroxy carboxylic acid used here, it is 3-hydroxybutyric acid, 4-hydroxybutyrate, 2-hydroxy-n-butyric acid, and 2-hydroxy- . The homopolymers and copolymers of hydroxycarboxylic acid, such as 3 and 3-dimethyl butanoic acid, 2-hydroxy-3-methyl butanoic acid, 2-methyl lactic acid, and a 2-hydroxy caproic acid, are mentioned.

[0017] As aliphatic series diol used for aliphatic series polyester or aliphatic series aromatic polyester, ethylene glycol, 1,4-butanediol, 1, and 4-cyclohexane dimethanol etc. is mentioned. Moreover, as aliphatic series dicarboxylic acid, a succinic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc. are mentioned, and a terephthalic acid, isophthalic acid, etc. are mentioned as aromatic series dicarboxylic acid. The aliphatic series polyester obtained by condensing these aliphatic series diols and aliphatic series dicarboxylic acid and the aliphatic series aromatic polyester obtained by condensing aliphatic series diol, aliphatic series dicarboxylic acid, and aromatic series dicarboxylic acid choose and carry out condensation polymerization of the one or more kinds out of each above-mentioned compound, respectively, further, can jump up with an isocyanate compound etc. if needed, and can obtain a desired polymer.

[0018] The aliphatic series polyester which carried out ring opening polymerization of the annular lactone is obtained as an annular monomer by carrying out the polymerization of one kind, such as epsilon-caprolactone, delta-valerolactone, and a beta-methyl-delta-valerolactone, or more than it. As synthetic system aliphatic series polyester, a copolymer with a cyclic anhydride, oxiranes, for example, a succinic anhydride and ethyleneoxide, propylene oxide, etc. is mentioned.

[0019] As aliphatic series polyester by which a biosynthesis is carried out within a fungus body, the aliphatic series polyester a biosynthesis is carried out [polyester] by acetyl-coenzyme A (acetyl CoA) within fungus bodies including *Alcaligenes YUTOROFASU* is mentioned. Although the aliphatic series polyester by which a biosynthesis is carried out within this fungus body is mainly poly-beta-hydroxybutyric acid (Pori 3HB), it is industrially advantageous to copolymerize a hydroxy valeric acid (HV) and to make it the copolymer of Pori (3 HB-CO-3HV) for the improvement in a practical use property as plastics. Generally 0-40-mol% of HV copolymerization ratio is desirable. Furthermore, long-chain hydroxy alkanoate, such as 3-hydroxy hexanoate, 3-hydroxy octanoate, and 3-hydroxyoctadecanoate, may be copolymerized instead of a hydroxy valeric acid.

[0020] In this invention, it is important to form a sheet from the resin constituent which blended polylactic acid system resin and specific polyester at a predetermined rate, and to carry out preliminary crystallization of this sheet. By carrying out preliminary crystallization, polylactic acid system resin can be crystallized in part at least, and the rigid grant to a Plastic solid is possible. Moreover, the drawdown at the time of shaping can be prevented as the degree of crystallinity of polylactic acid system resin is 20% or more. It is infinite about the degree of crystallinity of polylactic acid system resin, and you may crystallize 100% by preliminary crystallization. In addition, the general sheet formation approach can be used for the approach of forming a sheet from a resin constituent, for example, it can manufacture it by extrusion molding by T pressure die casting. However, hygroscopicity is high, and since hydrolysis nature is also high, polylactic acid system resin needs the moisture management in a production process, and when carrying out extrusion molding using a common 1 shaft extruder, after absorbing moisture and drying by a vacuum dryer etc., it produces a film. Moreover, when carrying out extrusion molding using a vent type twin screw extruder, since the dehydration effectiveness is high, efficient film production is possible, and it is also possible to consider as the multilayer sheet by two or more extruders. As the

preliminary crystallization approach, although there is especially no limit, the method of making the approach of carrying out fixed time amount heating continuously by the infrared heater, hot blast, etc., for example, a roll, etc. contact etc. is mentioned. It is desirable from a viewpoint of productivity to perform preliminary crystallization by contacting the sheet extruded by T pressure die casting on a hot cast roll.

[0021] The biodegradability sheet of this invention is excellent in fabrication nature, is the temperature which does not need warming of metal mold, and can be fabricated by the short molding cycle. Below, the shaping approach of this invention is explained. The biodegradability sheet of this invention can form a Plastic solid using the various shaping approaches, such as a vacuum forming, pressure forming, vacuum pressure sky shaping, and press forming. However, as for the molding temperature of a sheet, it is desirable that it is under the melting point of the polylactic acid system resin to blend more than the melting point of polyester. A problem may arise that molding temperature may become inadequate [thermal resistance or fabrication nature] for it to be under the melting point of polyester, and it is more than the melting point of polylactic acid system resin to rigidity or fabrication nature. Thus, if the biodegradability sheet of this invention is used, even if it does not hold metal mold to the temperature near the crystallization of polylactic acid system resin (for example, 80-130 degrees C), it is temperature lower than this temperature, and a Plastic solid can be formed by the short molding cycle. Moreover, the acquired Plastic solid is excellent also in thermal resistance and shock resistance. Some polylactic acid system resin [at least] crystallizes by preliminary crystallization, and the biodegradability sheet of this invention is mixed stock with other polyester, and this is considered because it has unique viscoelasticity. The relation between the dynamic viscoelasticity (E') of 1 operation gestalt of the biodegradability sheet of this invention and temperature is shown in drawing 1 . In drawing 1 , although the biodegradability sheet of this invention can be fabricated at the temperature between the glass transition temperature of ** polylactic acid system resin, and the melting point of ** polylactic acid system resin, it is desirable to fabricate at the temperature of more than the melting point of ** polyester and under the melting point of ** polylactic acid system resin. Moreover, since some polylactic acid system resin [at least] is crystallizing by preliminary crystallization, the crystal of the remaining polylactic acid system resin is urged, and shaping by the short molding cycle is possible, and the degree of crystallization of the acquired Plastic solid is also enough, and it has good thermal resistance.

[0022] As a Plastic solid formed using the biodegradability sheet of this invention, trays for electronic-parts conveyance, such as hot philharmonic containers, such as containers for a package, such as the tray and cup of food grades, such as a lunch box, and a fresh fish, prime meat, vegetables and fruits, tofu, a daily dish, dessert instant noodles, and a gear-tooth brush, a cell, drugs, cosmetics, and pudding Jammu Calais, or IC, transistor diode, etc., a carrier tape, etc. are mentioned, for example. Moreover, in this invention, a secondary additive can be added to the resin constituent used for formation of a biodegradability sheet, and various reforming can be performed. As a secondary additive, a stabilizer, an antioxidant, an ultraviolet ray absorbent, a pigment, *****, an electric conduction agent, a release agent, a plasticizer, perfume, an antimicrobial agent, a nucleation agent, other likes, etc. are mentioned, for example.

[0023]

[Example] Although an example, the example of a comparison, etc. are shown below and this invention is explained in full detail below, this invention does not receive a limit at all by these. In addition, the physical-properties value in an example and the example of a comparison evaluated by measuring by the following approaches.

A measuring method and the evaluation approach (1) The Plastic solid acquired from the heat-resistant evaluation biodegradability sheet was heat-treated for 20 minutes at 80 degrees C in hot blast circuit system oven, and the rate of volume reduction of a Plastic solid (%) was computed by the following formula.

The rate of volume reduction = using the hydro shot impact tester (form HTM- 1) by the evaluation Oriental energy machine company of { 1-(Plastic solid volume before Plastic solid volume / heat treatment after heat treatment)} x100(2) shock-resistance **, at the temperature of 23 degrees C, the

impact core whose diameter is 1/2 inch was made to collide with a biodegradability sheet at the rate of 3 m/sec, and the energy which destruction took was computed.

(3) Filled up with water the Plastic solid acquired from the evaluation biodegradability sheet of shock-proof **, carried out the seal of the opening, it was made to fall on concrete from height of 1m, and the existence of breakage of a Plastic solid was investigated.

(4) Based on measurement JIS-K-7121 of glass transition temperature, the programming rate measured the glass transition temperature of polyester by 10 degrees C / min with the differential scanning calorimetry (DSC).

(5) Based on measurement JIS-K -7121 of degree of crystallinity, with the differential scanning calorimetry (DSC), the programming rate measured the amount of heat of fusions (ΔH_m) and the amount of heat of crystallization (ΔH_c) resulting from the polylactic acid system resin in a biodegradability sheet, and computed the degree of crystallinity of polylactic acid system resin by the following type at 10 degrees C / min.

Pressure forming (pneumatic pressure: 2kg/cm²) was performed using the shaping metal mold (die temperature of 25 degrees C) of evaluation phi100mm of degree-of-crystallinity (%) = ($\Delta H_m - \Delta H_c$) / (polylactic acid system resin in 92.8x sheet comparatively) x100 (6) moldability, a depth of 30mm, and a contraction ratio 0.3, the mold size enlargement condition of a Plastic solid was observed, and the three-stage estimated. The valuation basis showed [the case where the Plastic solid of a good gestalt was formed] the case of the Plastic solid of "***" and a defect configuration for the case of level extent in which "O" and practical use are possible by "x."

[0024] (Example 1) It put into the 500L batch type polymerization tank equipped with an agitator and heating apparatus for what added 15 ppm of octylic acid tin to PYURAKKU Japan L-lactide (trade name-URASORB L) 100kg. The nitrogen purge was performed and the polymerization was performed for 60 minutes by 185 degrees C and agitating speed 100rpm. Having supplied the obtained melt to the 40mmphi said direction biaxial extruder equipped with three steps of vacuum vents by Mitsubishi Heavy Industries, LTD., and devolatilizing it by vent ** 4torr, at 200 degrees C, it extruded in the shape of a strand, and pelletized. The weight average molecular weight of the obtained polylactic acid system resin was 200,000, and the L body content was 99.5%. Moreover, the melting point by DSC was 171 degrees C. Mixed polybutylene succinate (Showa High Polymer trade-name "Bionolle 1001" melting-point: 111 degree C, a glass transition point: -40 degrees C) with the above-mentioned polylactic acid system resin as biodegradability aliphatic series system polyester at polylactic acid system resin / biodegradability aliphatic series system polyester = 60 % of the weight / 40% of the weight of a rate, and supplied this direction twin screw extruder, carried out melting kneading, and it was made to breathe out in the shape of a strand, it cut by the pelletizer, and the pellet was obtained. Subsequently, after having supplied the single screw extruder after drying the obtained pellet at 70 degrees C for 8 hours, and extruding from a T die, the 110-degree C cast roll was made to contact, and the biodegradability sheet with a thickness of 400 micrometers was obtained. The degree of crystallinity of the polylactic acid system resin of the obtained biodegradability sheet was 44%. Next, the Plastic solid was formed using the obtained biodegradability sheet. That is, using shaping metal mold (die temperature of 25 degrees C), pressure forming was performed under conditions with a sheet temperature [of 140 degrees C], and a pneumatic pressure of 2kg/cm², and the Plastic solid of biodegradability was acquired. About the acquired Plastic solid, evaluation of thermal-resistance and shock resistance **, shock-proof **, and a moldability was performed. The result is shown in Table 1.

[0025] (Example 2) The biodegradability sheet was obtained like the example 1 except having changed the loadings of polylactic acid system resin and biodegradability aliphatic series polyester to polylactic acid system resin / biodegradability aliphatic series system polyester = 50 % of the weight / 50% of the weight. The degree of crystallinity of the polylactic acid system resin of the obtained biodegradability sheet was 43%. Moreover, the Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 1.

[0026] (Example 3) The biodegradability sheet was obtained like the example 1 except having changed

the loadings of polylactic acid system resin and biodegradability aliphatic series polyester to polylactic acid system resin / biodegradability aliphatic series system polyester =40 % of the weight / 60% of the weight. The degree of crystallinity of the polylactic acid system resin of the obtained biodegradability sheet was 44%. Moreover, the Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 1.

[0027] (Example 4) The biodegradability sheet was obtained like the example 1 except having considered as polylactic acid system resin / biodegradability aliphatic series system polyester =70 % of the weight / 30 % of the weight, using polybutylene horse mackerel peat terephthalate ("Ecoflex" melting-point:109 degree C by BASF A.G., a glass transition point: -30 degrees C) as biodegradability aliphatic series system polyester. The degree of crystallinity of the polylactic acid of the obtained biodegradability sheet was 40%. Moreover, the Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 1.

[0028] (Example 5) It put into the 500L batch type polymerization tank equipped with an agitator and heating apparatus for what added 15 ppm of octylic acid tin to PYURAKKU Japan L-lactide (trade name-URASORB L) 90kg and company DL-lactide (trade name-URASORB DL) 10kg. The nitrogen purge was performed and the polymerization was performed for 60 minutes by 185 degrees C and agitating speed 100rpm. Having supplied the obtained melt to the Mitsubishi Heavy Industries 40mmphi said direction biaxial extruder equipped with three steps of vacuum vents, and devolatilizing it by vent ** 4torr, at 200 degrees C, it extruded in the shape of a strand, and pelletized. The weight average molecular weight of the obtained polylactic acid system resin was 200,000, and the L body content was 94.8%. Moreover, the melting point by DSC was 165 degrees C. After having mixed polybutylene succinate ("Bionolle 1001" melting-point:111 degree C by Showa High Polymer Co., Ltd., glass transition temperature: -40 degrees C) with this polylactic acid system resin as biodegradability aliphatic series system polyester at polylactic resin / biodegradability aliphatic series system polyester =50 % of the weight / 50 % of the weight, having supplied this direction twin screw extruder, carrying out melting kneading and making it breathe out in the shape of a strand, it cut by the pelletizer and the pellet was obtained. After drying the obtained pellet at 70 degrees C for 8 hours, supplied the single screw extruder, extruded from the T die, the 110-degree C cast roll was made to contact, and the biodegradability sheet with a thickness of 400 micrometers was obtained. The degree of crystallinity of the polylactic acid system resin of the obtained biodegradability sheet was 36%. The Plastic solid was formed using the obtained biodegradability sheet. That is, using shaping metal mold (die temperature of 25 degrees C), pressure forming was performed under conditions with a sheet temperature [of 140 degrees C], and a pneumatic pressure of 2kg/cm2, and the Plastic solid of a biodegradability sheet was acquired. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 1.

[0029] (Example 6) After having supplied the pellet obtained in the example 1 to the single screw extruder after drying at 70 degrees C for 8 hours, and extruding it from a T die, the 40-degree C cast roll was made to contact, and the biodegradability sheet with a thickness of 400 micrometers was obtained. The degree of crystallinity of the polylactic acid system resin of the obtained biodegradability sheet was 10%. The Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 1.

[0030] (Example 7) It put into the 500L batch type polymerization tank equipped with an agitator and heating apparatus for what added 15 ppm of octylic acid tin to PYURAKKU Japan L-lactide (trade name-URASORB L) 100kg. The nitrogen purge was performed and the polymerization was performed for 60 minutes by 185 degrees C and agitating speed 100rpm. Having supplied the obtained melt to the 40mm[by Mitsubishi Heavy Industries, LTD.] phi said direction biaxial extruder equipped with three steps of vacuum vents, and devolatilizing it by vent ** 4torr, at 200 degrees C, it extruded in the shape of a strand, and pelletized. The weight average molecular weight of the obtained polylactic acid system

resin was 130,000, and the L body content was 99.5%. Moreover, the melting point by DSC was 171 degrees C. After having mixed polybutylene succinate (trade-name "Bionolle 1001" melting-point: 111 degree C by Showa High Polymer Co., Ltd., a glass transition point: -40 degrees C) with the obtained polylactic resin as biodegradability aliphatic series system polyester at polylactic acid system resin / biodegradability aliphatic series system polyester = 60 % of the weight / 40 % of the weight, having supplied this direction twin screw extruder, carrying out melting kneading and making it breathe out in the shape of a strand, it cut by the pelletizer and the pellet was obtained. After drying the obtained pellet at 70 degrees C for 8 hours, supplied the single screw extruder, extruded from the T die, the 40-degree C cast roll was made to contact, and the biodegradability sheet with a thickness of 400 micrometers was obtained. The obtained biodegradability sheet was heat-treated within 110-degree C oven for 24 hours, and the sheet whose degree of crystallinity of polylactic acid system resin is 52% was obtained. The Plastic solid was formed using this biodegradability sheet. That is, using shaping metal mold (die temperature of 25 degrees C), under conditions with a sheet temperature [of 140 degrees C], and a pneumatic pressure of 2kg/cm², pressure forming was performed and the Plastic solid of biodegradability was acquired. Moreover, the Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 1.

[0031] (Example 1 of a comparison) After having supplied the polylactic acid system resin used in the example 1 to this direction twin screw extruder, carrying out melting kneading and making it breathe out in the shape of a strand, it cut by the pelletizer and the pellet was obtained. Supplied the above-mentioned pellet after 8-hour desiccation and to a single screw extruder at 70 degrees C, extruded from the T die, the 110-degree C cast roll was made to contact, and the biodegradability sheet with a thickness of 400 micrometers was obtained. The degree of crystallinity of the polylactic acid system resin of the obtained biodegradability sheet was 43%. Moreover, the Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 2.

[0032] (Example 2 of a comparison) The biodegradability sheet was produced like the example 1 except having changed the blending ratio of coal of polylactic acid system resin and biodegradability aliphatic series polyester to polylactic resin / biodegradability aliphatic series system polyester = 80 % of the weight / 20% of the weight. The degree of crystallinity of the polylactic acid of the obtained biodegradability sheet was 44%. Moreover, the Plastic solid was acquired like the example 1 using the obtained biodegradability sheet. About the acquired Plastic solid, the same evaluation as an example 1 was performed. The result is shown in Table 2.

[0033] (Example 3 of a comparison) In the example 1, the biodegradability sheet was produced like the example 1 except having considered as polylactic acid system resin / polyester = 70 % of the weight / 30 % of the weight, using polyhydroxy butyrate ("BIOGURIN" melting-point: 180 degree C by Mitsubishi Gas Chemical Co., Inc., a glass transition point: 4 degrees C) as biodegradability aliphatic series system polyester. The degree of crystallinity of the polylactic acid of the obtained biodegradability sheet was 41%. Moreover, although the Plastic solid was produced like the example 1 using the obtained biodegradability sheet, the ***** of a Plastic solid was extremely bad and was not able to acquire a Plastic solid. Therefore, thermal resistance etc. was not able to be evaluated.

[0034]

[Table 1]

		単位	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	実施例 7
構成比	A	重量%	60	50	40	70	50	60	60
	B		40	50	60	30	50	40	40
	結晶化度	%	44	43	44	40	36	10	52
	成形温度	℃	140	140	140	140	140	140	140
耐熱性	容積減容率	%	0.2	0.0	0.0	0.4	0.1	0.2	0.1
	耐衝撃性①	Kgf・mm	167	227	308	180	201	152	143
	耐衝撃性②	—	破壊せず	破壊せず	破壊せず	破壊せず	破壊せず	破壊せず	破壊せず
成形性	成形体の型脱形性	—	○	○	○	○	○	○	○

◆ A：ポリ乳酸樹脂 B：生分解性脂肪族系ポリエステル

◆ 結晶化度：生分解性シート中のポリ乳酸樹脂の結晶化度

◆ 成形温度：成形時の生分解性シートの温度

[0035]

[Table 2]

		単位	比較例 1	比較例 2	比較例 3
構成比	A	重量%	100	80	70
	B		0	20	30
	結晶化度	%	42	43	41
	成形温度	℃	140	140	140
耐熱性	容積減容率	%	53.1	7.8	—
	耐衝撃性①	Kgf・mm	17	85	—
	耐衝撃性②	—	割れ	破壊せず	—
成形性	成形体の型脱形性	—	×	△	×

[0036] Table 1 and 2 to the examples 1-6 -- thermal resistance, shock resistance, and a moldability -- all were found by that a good Plastic solid is acquired by the usual molding cycle satisfactory. On the other hand, in the example 1 of a comparison, since biodegradability aliphatic series system polyester is not contained, there is thermal resistance, a problem is in shock resistance, and a Plastic solid that mold size enlargement nature of a Plastic solid is inadequate and good was not acquired. Since there were few loadings of biodegradability aliphatic series system polyester, the problem was in thermal resistance, and the example 2 of a comparison of the mold size enlargement nature of a Plastic solid as well as the example 1 of a comparison was inadequate. In addition, the drawdown of a sheet was not produced when the condition of the drawdown of a sheet was also observed in evaluation of a moldability about the Plastic solid of an example 1.

[0037]

[Effect of the Invention] As explained in detail above, it is not necessary to hold metal mold in the sheet

of this invention near the crystallization of polylactic acid system resin (80-130 degrees C), the Plastic solid which has thermal resistance also with the metal mold of ordinary temperature is acquired, and shaping by the usual molding cycle is possible. that is, according to this invention, special equipments, such as a facility for warming that ** molding cycle which was the conventional trouble becomes long, and a manufacturing cost becomes high by using the preliminary crystallization sheet of polylactic acid system resin and specific polyester for shaping, and ** metal mold, are required -- etc. -- a problem is solved and the biodegradability sheet in which various shaping of a vacuum forming, pressure forming, vaccum pressure sky shaping, press forming, etc. is possible can be offered. Moreover, the Plastic solid excellent in thermal resistance, shock resistance, and a moldability and its shaping approach can be offered using this biodegradability sheet.

[Translation done.]